

PATENT APPLICATION
Navy Case No. 83,068

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION FOR LETTERS PATENT

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN THAT Karen Swider Lyons and Debra R. Rolison who are citizens of the United States of America, and are residents of, Arlington, VA, invented certain new and useful improvements in "METHOD TO PREPARE DEFECTIVE METAL OXIDES WITH INCREASED SPECIFIC CAPACITY" of which the following is a specification:

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TITLE

Method to prepare defective metal oxides with increased specific capacity

BACKGROUND OF THE INVENTION

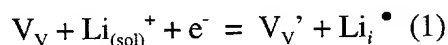
1. Field of the Invention

The present invention relates generally to improved capacity of defective materials and more specifically to the preparation of defective metal oxides for battery cathodes with increased specific energy and improved lithium capacity.

2. Discussion of the Background

The revolution in the portable electronics industry has increased the demand for lightweight, high-energy batteries. Strategies for improving the energy density of batteries include technical challenges such as (1) increasing the voltage difference between the cathode and anode, (2) decreasing the weight of the materials, and (3) increasing the charge-storage capacity of the materials.

The obstacles to these improvements are often physical. For instance, the lithium (Li) capacity of metal-oxide charge-storage materials is limited because the valence of the metal cations fixes the number of electrons withdrawn from each metal center, as shown for the V_2O_5 -cathode half-cell reaction in Eq. 1. Only one electron is consumed when a lithium ion from an electrolyte solution ($Li_{(sol)}^+$) inserts into a V_2O_5 cathode and a V^{5+} ion is reduced to V^{4+} (Eq. 1).



Using Kröger-Vink notation, V_v designates a V^{5+} ion at a vanadium-cation site in the V_2O_5 lattice, and V_v' represents the occupation of the cation site with a V^{4+} ion, leaving it effectively 1-negative ($'$). Li_i^\bullet represents a lithium ion that is located in an interstitial site (i) and has an effective 1-positive charge ($^\bullet$). The Li^+ may actually be associated with an oxygen anion, but this defect is electrically and site equivalent to a lithium interstitial. Kröger-Vink notation, which is used to write equilibrium reactions and mass action equations in defective oxides, is also useful for writing equations for the metal oxides used in batteries, because it demands site and charge balance in addition to chemical balance and includes defects (vacancies, etc.) as chemical species.

The vanadium cations in bulk V_2O_5 are reduced to an average oxidation state of +4.5 with Li^+ insertion, because structural constraints allow reduction of only half of the V^{5+} ions to V^{4+} . This physical limitation of 0.5 electron stored per vanadium ion is broken when Li^+ is inserted into V_2O_5 materials synthesized by sol-gel methods. Up to 2.5 Li^+ can be inserted per vanadium ion into the amorphous, high surface area, high porosity frameworks of V_2O_5 aerogels and xerogels, resulting in capacities as high as 600 mAh/g. Although Eq. (1) predicts V^{3+} defects should be formed when 3 to 5 equivalents of Li^+ are inserted into V_2O_5 xerogels and aerogels, X-ray absorption spectroscopy (XAS) studies indicate that only V^{4+} and V^{5+} ions are present in the fully discharged materials. Raman spectroscopy shows unique vibrational bands in $Li-V_2O_5$ xerogels, but provides no identification of the mechanism for the additional Li^+ insertion. Even if the metal-oxide materials become metallic, the charge balance constraints in Eq. 1 still apply.

SUMMARY OF THE INVENTION

5 The present invention has been made in view of the above-described problems that need to be solved, and an object of the present invention is therefore to provide a method to improve the lithium capacity of metal oxide materials. Point defects are introduced into a metal oxide to increase its lithium ion capacity.

10 Accordingly, it is one object of the present invention to provide a novel method for the preparation of defective metal oxides for battery cathodes with increased capacity.

It is another object of this invention to provide a method for the preparation, using a heat treatment, of defective metal oxides for battery cathodes with increased capacity.

15 It is another object of this invention to provide a method for the preparation, by using a chemical treatment, of defective metal oxides for battery cathodes with increased capacity.

It is another object of this invention to provide a method for the preparation of defective metal oxides for battery cathodes with increased capacity.

20 These and other objects, which will become apparent during the following detailed description, have been achieved by the inventors' discovery that lithium-ion capacity of metal oxides may be controlled via point defects that may be introduced into a metal oxide by:

- (a) applying a mixture of O_2 and H_2O gas to a sufficient amount of a V_2O_5 metal oxide sample at a linear flow rate of about 50 - 350 cm;
- (b) heating the metal oxide sample at a temperature of about 300 - 600 °C for a time period of about 6 - 72 hours; and
- 5 (c) cooling the metal oxide sample.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention and many of the attendant advantages thereof will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings, wherein:

FIG. 1 is an illustration of X-ray diffraction (XRD) patterns of V_2O_5 samples as received and after heating under different gas mixtures. The different samples shown are (a) as received, and after heating under (b) O_2 , (c) O_2/H_2O , (d) Ar, and (e) Ar/ H_2O .

15 FIG. 2 is an illustration of charge-discharge profiles of 0.5 mg V_2O_5 electrodes after treatment by heating under different atmospheres (A) first complete charging cycle (10 μA), (B) first complete discharge cycle (10 μA).

FIG. 3 is a table showing a series of V_2O_5 samples heated under different atmospheres: capacity of 0.5 mg samples at discharge rate of 10 μA , and open-circuit potential (OCP)
20 of the materials before cycling.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Thus, in a first embodiment, the present invention provides for

- (a) applying a mixture of O_2 and H_2O gas to a sufficient amount of a V_2O_5 metal oxide sample at a linear flow rate of about 50 - 350 cm;
- (b) heating said metal oxide sample at a temperature of about 300 - 600 °C for a time period of about 6 - 72 hours; and
- (c) cooling said metal oxide sample.

Vacancies may be introduced into the vanadium oxide (V_2O_5) lattice during heating under various atmospheric conditions. It is to be understood that " V_2O_5 " describes vanadium oxide in which the vanadium is predominantly in the +5 valence state.

To examine the interaction of Li^+ with defects in the V_2O_5 lattice, commercially available, anhydrous, bulk V_2O_5 is made defective by conventional heat treatments under O_2 , O_2/H_2O , Ar, and Ar/ H_2O , and the treated materials are tested for changes in Li capacity relative to the as-received V_2O_5 powder. Although bulk V_2O_5 usually has lower capacity than materials synthesized from sol-gels, it is compositionally uniform and stable, and therefore an ideal standard material.

A range of defective V_2O_5 materials is prepared by heating commercial V_2O_5 powder (Alfa) under O_2 , O_2/H_2O , Ar, and Ar/ H_2O . Approximately 1 g of the as-received V_2O_5 powder is loaded into an alumina boat in a 1" diameter alumina tube under ~350 ccm

flowing O_2 , O_2/H_2O , Ar, or Ar/H_2O and heated at $5\text{ }^\circ\text{C/min}$ to $460\text{ }^\circ\text{C}$. After holding at $460\text{ }^\circ\text{C}$ for 24 h, the samples are cooled at $5\text{ }^\circ\text{C/min}$ to room temperature and then stored in sealed vials under ambient air.

The structure of the V_2O_5 samples is determined via XRD (Rigaku Rotoflex, Cu rotating anode, 50 kV and 150 mA). Powder samples are mounted with double-stick tape on glass slides. Electrodes are prepared by vigorously mixing the V_2O_5 with 13 wt% acetylene black (Alfa), 9 wt% polyvinylidene fluoride (PVDF, Elf Atochem) in an excess of either 2-methyl pentanone (Aldrich) at $60\text{ }^\circ\text{C}$ or hexanes (Aldrich) at room temperature. The suspension is added dropwise to a strip of clean Pt foil and heated on a hot plate to remove excess solvent. The amount of material on the foil (0.5 to 1.5 mg) is then adjusted so that the V_2O_5 weight in all samples is within $\pm 2\%$. After vacuum drying at $> 150\text{ }^\circ\text{C}$ for 12 to 24 h, the electrodes are loaded into an Ar-filled glove box. The V_2O_5 /Pt electrodes are tested in a solution of 1 M Li-perchlorate (Aldrich) in distilled propylene carbonate (Aldrich) vs Li metal auxiliary and reference electrodes (Aldrich). The electrodes are charged and discharged between 2 and 4 V vs Li using a potentiostat (PAR 263; M270 software) in galvanostatic mode. The open-circuit potential (OCP) of each electrode is measured after equilibrating for at least 10 min in the Li-propylene carbonate electrolyte. The samples are first charged to 4 V to displace residual protons before discharging to 2 V. Acetylene black and platinum electrodes with no V_2O_5 have negligible capacity when charged and discharged between 2 and 4 V.

X-ray diffraction shows that the as-received, orange-colored V_2O_5 is crystalline and has the Shcherbinaite structure (ICCD PDF Card # 41-1426). The same phase is measured for the samples heated at 460 °C under O_2 , O_2/H_2O , and Ar (Fig. 1), indicating that the long-range structure of the V_2O_5 is not affected by these temperature/atmosphere/time conditions and suggesting that ionic defects have been introduced. All of these samples are also orange-colored after reacting under heat. The XRD pattern of the green-black Ar/ H_2O -heated V_2O_5 indicates that it is highly disordered to amorphous and has only a trace of the Shcherbinaite structure. Additional peaks are measured in the Ar/ H_2O -heated V_2O_5 but these diffraction peaks cannot be matched to a single vanadium-oxide or hydrous vanadium-oxide phase.

The Li capacity of V_2O_5 powder is significantly affected by the heating conditions. Figure 2 shows a series of electrodes that contain 0.5 mg of V_2O_5 that are charged and discharged at 10 μA (20 $\mu A/mg$); the Li capacity results are summarized in Table I. Under these charging and discharging conditions, the capacity of the Ar/ H_2O -heated V_2O_5 is 72 mA·h/g ($\pm 4\%$), which is almost 58% lower than the capacity of the as-received V_2O_5 (172 mA·h/g). The capacity of the O_2/H_2O -heated V_2O_5 is 212 mA·h/g, or 22% greater than the capacity of the as-received V_2O_5 . The capacities of the Ar-heated and O_2 -heated V_2O_5 are 8% and 25% lower than that of the as-received V_2O_5 , respectively. The profiles of the charge and discharge curves are identical for the samples heated under O_2 , O_2/H_2O , and Ar versus the as-received V_2O_5 , however the time (or capacity) of each charge and discharge potential step varies.

The values measured for the Li capacities vary between different batches of electrodes probably due to variations in the sample weights (or electrode thicknesses) and drying conditions. However, the same trends are observed. Also, the differences in the capacities of the V_2O_5 materials are lessened as they are discharged at higher rates (up to 100 $\mu A/mg$). The capacity of all of the V_2O_5 powders fades by 1 to 3 % after each cycle. The acetylene black and platinum make negligible contributions to the results.

In comparison to the as-received V_2O_5 , the OCPs of the O_2 - and Ar-heated V_2O_5 are ~ 65 mV higher, the O_2/H_2O -heated V_2O_5 is 50 mV higher, and the Ar/ H_2O -heated material is only ~ 5 mV higher. The OCP values vary between electrode batches, but the trend remains the same.

Heating bulk V_2O_5 under O_2 , O_2/H_2O , and Ar causes no change to the long-range structure of the metal oxide, but it significantly affects the V_2O_5 lithium capacity. Under the O_2 , Ar, and Ar/ H_2O heating steps, the Li capacity is decreased. The lithium capacity is increased for the samples heated under O_2/H_2O . Since the long-range structure does not change, this suggests that local ionic defects introduced by the O_2/H_2O heat treatment, such as cation vacancies, are affecting the lithium capacity of the metal oxide.

The V_2O_5 that is heated under Ar/ H_2O has ~60% decrease in Li capacity versus the as-received material, but it also undergoes a phase transformation to a highly disordered, hydrous structure during temperature/atmosphere treatment. These results support the supposition that the high Li capacity of V_2O_5 materials prepared by sol-gel methods is not

just due to their hydrous, highly disordered structure, but rather to another effect such as ionic defects.

5 The change in the OCPs of the heated V_2O_5 materials indicates that they are thermodynamically different from the as-received material. It is suggested that other metal oxides behave similarly with O_2/H_2O heating. Examples of metal oxides include vanadium oxide, manganese oxide, nickel oxide, cobalt oxide, and iron oxide. The metal oxide can be in its stoichiometric or non-stoichiometric form. The metal oxide can be doped with a transition metal. Additionally, the lithiated form of the metal oxide can be used.

Hydrogen ions (i.e., protons and hydride ions) usually behave similarly to lithium ions. This approach is applicable to other battery systems using metal oxides, such as alkaline and metal hydride batteries.